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CITATION:

TANIHARA, Yoshifumi ...[et al]. <Preliminary>Biomimetic Oxidation of β -O-4 Lignin Model Compound with tert-Butylhydroperoxide and Fe(III)-Octacarboxyphthalocyanine. Wood research : bulletin of the Wood Research Institute Kyoto University 1994, 8 ...

ISSUE DATE:

1994-09-30

URL:

<http://hdl.handle.net/2433/53253>

RIGHT:

Biomimetic Oxidation of β -O-4 Lignin Model Compound with *tert*-Butylhydroperoxide and Fe(III)-Octacarboxyphthalocyanine*¹

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(Received June 1, 1994)

Keywords: Biomimetic oxidation, phthalocyanine, catalyst, ligninase model, cleavage reaction.

Lignin-peroxidase mimetic oxidation of a lignin model compound was first reported by Shimada et al.¹⁾ with synthetic and natural porphyrin iron-complexes; the one-electron oxidation mechanism for the enzymatic reaction has been proposed²⁾. A hemin catalyst mimicked the lignin peroxidase (Lip) which catalyzes the C α -C β bond cleavage of β -1 model substrate (accompanied by oxygenation and deuterium retention)^{2,3)}, and the aromatic ring cleavage of veratryl (3, 4-dimethoxybenzyl) alcohol, yielding γ - and δ -lactone products^{4,5)}.

Recently, several laboratories have been investigating similar biomimetic oxidations of lignin models with more sophisticated water-soluble synthetic porphyrins⁶⁻¹¹⁾. It is particularly interesting to note that the selective oxidative cleavage of 1, 2-dimethoxyarenes to muconic diesters with relatively high yield was catalyzed by Fe(III)-sulfonated-tetrakis (pentafluorophenyl) porphyrin¹¹⁾.

We report here the first example of C α -C β bond cleavage and ring cleavage of β -O-4 model lignin model compound catalyzed by a water soluble Fe(III)-octacarboxyphthalocyanine (OcPc) complex¹²⁾, although the oxidation of monomeric lignin model compounds with various water-soluble metallophthalocyanines has been previously reported¹³⁾.

The reaction mixture (2 ml of water adjusted to pH 3) containing the β -O-4 model substrate (1, 10 μ mol), Fe-OcPc (1 μ mol), and *tert*-butylhydroperoxide (t-BuOOH), was incubated at room temperature for 30 min. The control system, lacking the Fe-OcPc catalyst, was incubated in the same way. After the incubation oxidation products were extracted with ethyl acetate and analyzed with GC-MS after acetylation of the dried

*¹ Part of this work was presented in the 36th Lignin symposium, held in Sapporo, Japan, in October, 1991.

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extracts; the products (II–VII) were identified by comparison of their spectra with those of the corresponding authentic compounds.

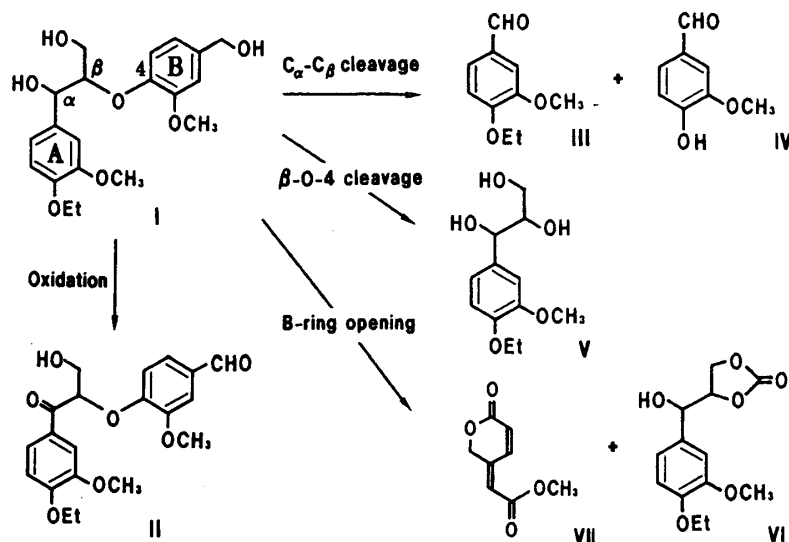


Fig. 1. LiP-mimetic Fe-octacarboxyphthalocyanine catalyzes oxidation of β -O-4 lignin model compound (I).

Fig. 1 shows that Fe-OcPc catalyzes the C α -C β cleavage of I (yielding the products III and IV), the β -O-4 ether cleavage, (yielding the product V), and the cleavage of B-ring of I (yielding products VI and VII). The control reaction system did not yield these products under the reaction conditions used, which indicates that t-BuOOH did not cause such cleavage reactions. It is noteworthy that VII was identified for the first time from the products formed from the β -O-4 lignin substructure model. Therefore, this finding prompted us to examine a possible formation of VII even in the Lip system. Eventually, we confirmed that VII was also produced from the Lip-catalyzed oxidation of I. The alternative experiment also demonstrated that the Fe-OcPc system is capable of catalyzing the ring cleavage of veratryl alcohol, yielding γ - and δ -lactones as the ring-opened products that were also produced from the Lip system⁴⁾.

These results clearly indicate that Fe-OcPc system like the metalloporphyrin systems simulates the activity of Lip in the cleavage patterns of both dimeric β -O-4¹⁴⁾, and monomeric lignin model substrates¹⁵⁾. Furthermore, it is noteworthy that Fe-OcPc also catalyzed the C α -C β bond cleavage of β -O-4 substrate (II), yielding IV and 4-O-ethylvanillic acid¹⁶⁾ because II is not utilized as substrate by the LiP system¹⁷⁾. Since the control reaction system did not produce these cleaved products, the possibility of participation of Vayer-Villiger type reaction was eliminated.

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